

# INFRARED TRANSMISSION OF $(R_2O \text{ OR } R'O)-(TiO_2, Nb_2O_5 \text{ OR } Ta_2O_5)-Al_2O_3$ GLASSES

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The new families of aluminate glasses obtained by the present authors from their melts in the systems  $K_2O-Ta_2O_5-Al_2O_3$ ,  $Na_2O-K_2O-Ta_2O_5-Al_2O_3$ ,  $K_2O-Cs_2O-Ta_2O_5-Al_2O_3$ ,  $K_2O-Nb_2O_5-Al_2O_3$ ,  $Na_2O-K_2O-TiO_2-Al_2O_3$ ,  $BaO-TiO_2-Al_2O_3$ ,  $BaO-ZrO_2-TiO_2-Al_2O_3$  and  $Na_2O-K_2O-BaO-Ta_2O_5-TiO_2-Al_2O_3$  showed high transmissions of visible and infrared (IR) radiation ranging from 0.4 to about 6  $\mu m$ , as well as high refractive indices up to 2.0. Their physical and chemical properties such as glass-forming ability, softening temperature, hardness and hygroscopicity were comparable to conventional silicate glasses. These properties are useful for IR applications. The cause of the high IR transmission of the aluminate glasses was interpreted in terms of the masses of the constituent cations and the single bond strengths of the cations with oxygen ions.

## 1. Introduction

The present authors recently obtained some new families of aluminate glasses from their melts in the systems  $K_2O-Nb_2O_5-Al_2O_3$ ,  $Cs_2O-Nb_2O_5-Al_2O_3$ ,  $K_2O-Ta_2O_5-Al_2O_3$ ,  $Cs_2O-Ta_2O_5-Al_2O_3$ ,  $Na_2O-TiO_2-Al_2O_3$ ,  $K_2O-TiO_2-Al_2O_3$  and  $BaO-TiO_2-Al_2O_3$  on a practically useful scale [1,2]. Up to that time the silica-free aluminate melts known to form glasses were only those based on the  $CaO-Al_2O_3$  system [3]. The glasses of the  $CaO-Al_2O_3$  system were reported to transmit to longer wavelengths in the infrared (IR) than the silicate glasses [4].

The present article is a systematic presentation of the results of measurement of the visible and IR transmissions as well as refractive indices of a series of glasses of the systems described above, and also of their modified systems. Their high IR transmissions are interpreted in terms of the masses of the constituent cations and bond strengths of the cations with oxygen ions.

The other properties such as density, thermal expansion coefficient, softening temperature, hardness and hygroscopicity, which are important for use as IR transmission optical lenses or filters, are also presented for one of the glasses.

## 2. Experimental

### 2.1. Glass preparation

Batch mixtures yielding the oxide composition (mol%) given in table 1 was prepared from reagent grade chemicals of  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$ ,  $\text{BaCO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$ . They were melted in 10–15 g amounts in a 30–50 ml Pt 10% Rh crucible covered with a Pt lid in a SiC furnace at 1550°C for 0.5–1 h. The melts were poured on to a steel plate and pressed into plates approximately 1–2 mm thick. They were then quickly put into a preheated electric furnace, annealed at 500°C for 30 min, and furnace-cooled.

Among the glasses prepared, glass 10 was found to be highly stable to devitrification during cooling from its melt; it could be easily cast into a clear disc 10 cm in diameter and 2 mm thick.

### 2.2. Visible and infrared transmission

The glass plates were cut into rectangular slabs,  $20 \times 10$  mm. They were abraded with  $\text{Al}_2\text{O}_3$  powder and finished with  $\text{CeO}_2$  powder to flat and parallel surfaces and to various thicknesses ranging from 0.5 to 1.5 mm. To obtain transmission curves in the same thickness (1.00 mm) for all the compositions, the transmissions of two glass plates of different thicknesses,  $x_1$  and  $x_2$ , were measured for each composition at respective wavelengths in the range from 0.4 to 7  $\mu\text{m}$ . The transmissions in the wavelength range from 0.4 to 2.5  $\mu\text{m}$  were measured on a Shimadzu recording spectrophotometer (model MPS-50L) and those from 2.5 to 7  $\mu\text{m}$  on a Hitachi infrared spectrometer (model EPI-S2). From the two transmission values  $T_1$  and  $T_2$  measured for the two plates of different thicknesses at respective wavelengths, the transmission  $T_3$  for

Table 1

Glass compositions (mol%).

No.	$\text{NaO}_{0.5}$	$\text{KO}_{0.5}$	$\text{CsO}_{0.5}$	$\text{BaO}$	$\text{ZrO}_2$	$\text{NbO}_{2.5}$	$\text{TaO}_{2.5}$	$\text{TiO}_2$	$\text{AlO}_{1.5}$
1	35.00								
2	40.00					35.00			30.00
3	42.50					40.00			20.00
4	17.50					42.50			15.00
5	22.50		22.50			35.00			30.00
6	42.50					32.50			22.50
7	17.50					42.50			15.00
8				25.00				40.00	25.00
9				25.00	16.50			50.00	25.00
10	9.37	9.37		12.46	4.12		19.83	33.50	25.00
								19.83	25.02

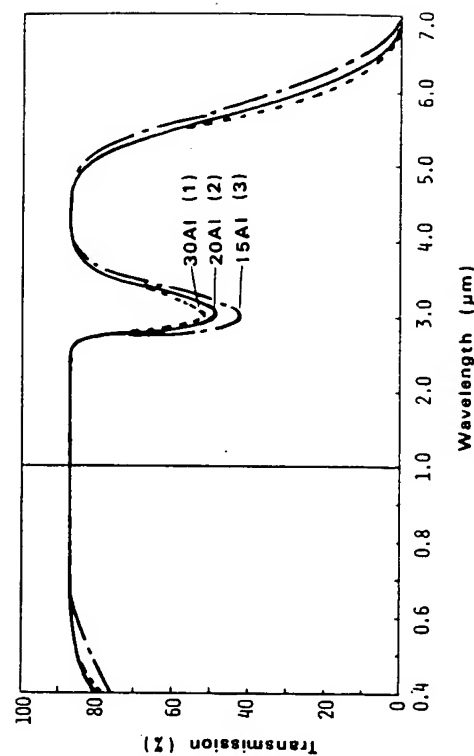


Fig. 1. Visible and IR transmissions of  $\text{K}_2\text{O}-\text{Ta}_2\text{O}_5-\text{Al}_2\text{O}_3$  glasses with varying  $\text{Al}_2\text{O}_3$  content ( $\text{K}_2\text{O}/\text{Ta}_2\text{O}_5 = 1$ , thickness 1 mm).

the thickness of 1.00 mm was estimated by using the relation

$$T(\%) = 100(1-R)^2 \exp(-\alpha x), \quad (1)$$

where  $T$  is the transmission,  $R$  is the reflectivity,  $\alpha$  is the absorption coefficient and  $x$  is the thickness of the specimen, i.e. the transmission  $T_3$  for the thickness of 1.00 mm was obtained by substituting the following equations in eq. (1).

$$x = 0.100 \text{ (cm)}, \quad \alpha = (\ln T_1 - \ln T_2)/(x_2 - x_1),$$

$$(1-R)^2 = \left(\frac{1}{100}\right) \exp[(x_2 \ln T_1 - x_1 \ln T_2)/(x_2 - x_1)].$$

The results are shown in figs. 1–4. For comparison, the transmissions of a commercial silica glass and a calcium aluminate glass of the composition reported by Hafner et al. [4] ( $1\text{A}5846$ :  $\text{NaO}_{0.5}$  7.5,  $\text{KO}_{0.5}$  2.5,  $\text{CaO}$  32.5,  $\text{AlO}_{1.5}$  57.5,  $\text{MgO}$  2.0,  $\text{BaO}$  2.0,  $\text{LaO}_{1.5}$  2.0,  $\text{FeO}_{1.5}$  2.0 mol%) were measured by the same method as described above and shown in fig. 5.

### 2.3. Refractive index and dispersion

Some of the glass plates (glasses 1, 2, 8, 9 and 10) were cut into a form of rectangular or triangle prism and polished with  $\text{CeO}_2$  powder. Their refractive indices  $n_D$  and  $n_F$  were measured at wavelengths of 0.6563, 0.5876 and 0.4861  $\mu\text{m}$ , respectively, with a Pülfich or a Hilger–Watts refractometer. The results are shown in table 2. Their Abbe numbers  $\nu = (n_D - 1)/(n_F - n_C)$  calculated from the refractive indices are also shown in table 2.

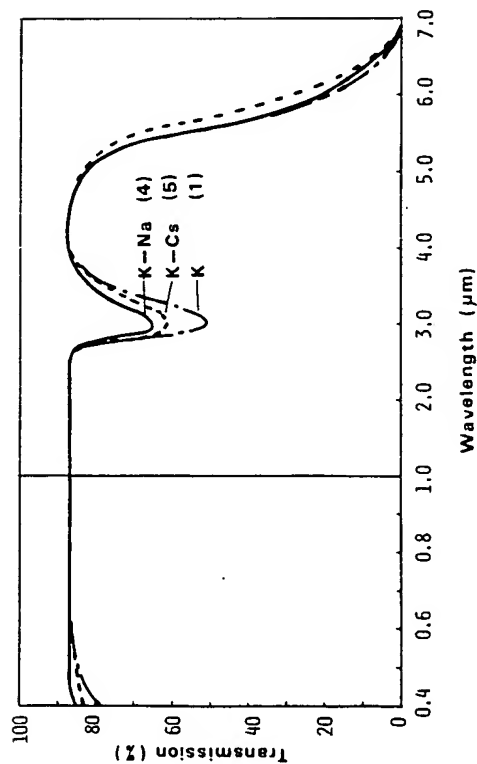


Fig. 2. Visible and IR transmissions of  $K_2O-Ta_2O_5-Al_2O_3$  and mixed alkaline oxides- $Ta_2O_5-Al_2O_3$  glasses (thickness 1 mm).

#### 2.4. Other physical and chemical properties

Glass 10 which could be obtained from its melt most easily among those given in table 1 was examined in the following properties.

- (1) Density measured by an Archimedean technique.
- (2) Thermal expansion measured with an extension rod dilatometer.

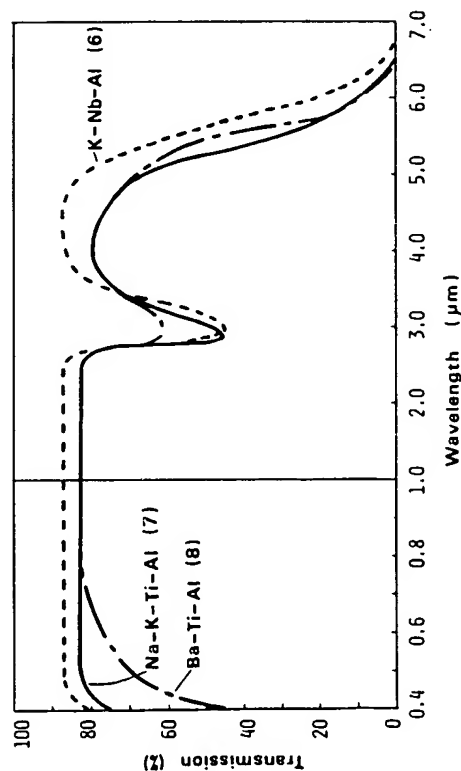


Fig. 3. Visible and IR transmissions of  $Nb_2O_5$ - or  $TiO_2$ - containing aluminate glasses (thickness 1 mm).

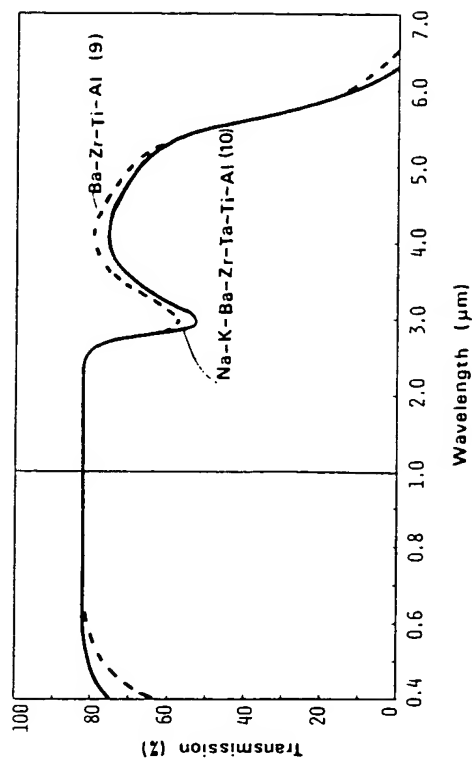


Fig. 4. Visible and IR transmissions of glasses 9 and 10 (thickness 1 mm).

- (3) Transition temperature determined on the thermal expansion curve.
  - (4) Incipient softening temperature determined on the thermal expansion curve.
  - (5) Vickers hardness measured with a Leitz small hardness tester (Durimet) using an indenter with a 50 g load.
  - (6) Hygroscopicity determined by measuring the amount of water absorbed by the powdered samples exposed for varying times [5].
- For determining the hygroscopicity, the glass was crushed in a steel motor and

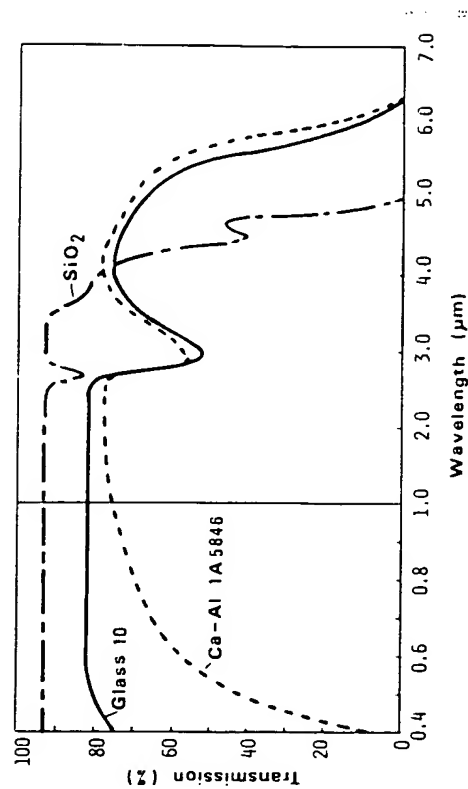


Fig. 5. Visible and IR transmissions of glass 10, silica glass and calcium aluminate glass 1A5846 [4] (thickness 1 mm).

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Table 2  
Refractive indices and Abbe numbers.

No.	$n_C$	$n_D$	$n_F$	$\nu$
1	1.724	1.734	1.740	46
2	1.724	1.734	1.740	46
8		2.010	2.045	
9		1.962	1.990	
10	1.893	1.903	1.928	26

Table 3  
Physical and chemical properties of glass 10.

density	4.73 g/cm <sup>3</sup>
thermal expansion coefficient (20–650°C)	$100 \times 10^{-7}/^\circ\text{C}$
transition temperature	670°C
incipient softening temperature	720°C
Vickers hardness	660 kg/mm <sup>2</sup>
water absorption	16 mg/cm <sup>3</sup> (after 1 h), 16 mg/cm <sup>3</sup> (after 2 h)
(cf. window glass)	32 mg/cm <sup>3</sup> (after 1 h), 37 mg/cm <sup>3</sup> (after 2 h)

passed through a no. 145 sieve with 0.105 mm opening and dried at 110°C. A 1 g sample of the powder, for a glass (glass 10) of density 4.73 or a proportional amount of a reference glass of different density, was then put in a shallow weighing bottle and exposed to 95% rh obtained by a saturated solution of Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O at 25°C, and the increase in a weight of the samples was determined. As a reference, a commercial window glass was used.

The results are shown in table 3. The physical and chemical properties of glass 10 are comparable to conventional silicate glasses.

## 3. Discussion

It can be seen from figs. 1–4 that all the glasses obtained by the present authors transmit well the visible and IR radiation ranging from 0.4 to 6.0  $\mu\text{m}$  in wavelength, except for near 3  $\mu\text{m}$ .

An absorption band near 3  $\mu\text{m}$  is commonly observed for silicate glasses and attributed to the O–H stretching vibrations of free OH groups contained in the glasses [6]. Since the wavelength of the absorption band observed near 3  $\mu\text{m}$  for the present aluminate glasses is almost independent of the composition of the glasses, this band is ascribed to the presence of the free OH group in the glasses. The intensity of this absorption was found to be reduced to a certain extent by mixing alkali oxides, as shown in fig. 2.

The 1 mm thick commercial silica glass transmits radiation only up to 5  $\mu\text{m}$  in wavelength, whereas all the aluminate glasses of the same thickness obtained by the present authors transmit radiation up to 6  $\mu\text{m}$  so well, as shown in figs. 1–5. The reasons for this are as follows.

The location of the cut-off wavelength in the IR region of an oxide glass is affected by various absorptions such as those due to the fundamental cation–oxygen ions stretching vibrations, their overtone vibrations, water bands, etc. Among these, however, the fundamental cation–oxygen ion stretching vibrations would have the strongest effect since the strength of the fundamental absorption band is the greatest [7]. Thus, it can be said that the cutoff wavelength in the IR region of an oxide glass is mainly determined by the absorptions due to the fundamental cation–oxygen ion stretching vibrations. The same idea was already stated by Simon [7]; e.g. the fundamental absorption band from the Si–O stretching vibration, which has a maximum at  $\approx 9 \mu\text{m}$ , extends far into the high-frequency region and make its appearance as a familiar cutoff in the 3–5  $\mu\text{m}$  wavelength range in silicate glasses.

Among the cation–oxygen ion bonds in the present aluminate glasses, the fourfold coordinate Al–O [1,2] and the sixfold coordinated Ti–O [2] bonds are known to show the fundamental absorption bands due to their stretching vibrations at 11–14 and 15–20  $\mu\text{m}$ , respectively [8]. Although the wavelengths of the fundamental absorptions due to the other cation–oxygen ion stretching vibrations are unknown, they might be estimated qualitatively by using a theory of diatomic molecules [9], as follows. According to the theory, the wavelength  $\lambda$  of the fundamental absorption, due to the stretching vibration of a diatomic molecule, is given by the formula

$$\lambda = 2\pi c (\mu/f)^{1/2}, \quad (2)$$

where  $c$  is the light velocity,  $\mu$  is the reduced mass defined by  $m_1 m_2 / (m_1 + m_2)$ , where  $m_1$  and  $m_2$  are masses of the constituent atoms, and  $f$  is the force constant. Usually, a large force constant is an indication of a strong bond in a series of molecules belonging to the same type [9]. If it is accepted that the force constant is roughly proportional to the bond strength  $f'$  and, furthermore, that this relationship can be applied to the stretching vibrations of all of the cation–oxygen ion bonds in the glasses, the following equation is obtained.

$$\lambda' = (\mu'/f')^{1/2}, \quad (3)$$

where  $\lambda'$  is the relative measure of the wavelengths of the fundamental absorption bands due to the cation–oxygen ion stretching vibrations in the glasses, and  $\mu'$  is the reduced mass given by  $m_c m_o / (m_c + m_o)$ , where  $m_c$  and  $m_o$  are masses of the cations and oxygen ions in the glasses.

Table 4 shows the results of the calculations, using eq. (3), of the values of  $\lambda'$  for all the cation–oxygen ion stretching vibrations in the present aluminate glasses. For comparison, the calculated value of the Si–O vibration is also shown. For the calculations, the values of the strengths of the single cation–oxygen ion bonds in the oxide

Relative absorption wavelengths of cation-oxygen ion stretching vibrations.

Bond	Mass of cation $m_c$	Reduced mass $\mu (m_c m_o / (m_c + m_o))$	Dissociation energy, $E_d$ (kcal)	Coordination number $n$	Single bond strength $f'$ ( $E_d/n$ )	Relative absorption length $\lambda'$ ( $\mu f'$ ) <sup>1/2</sup>
Na-O	23.0	9.4	120	6	20	0.69
K-O	39.1	11.4	115	9	13	0.94
Ca-O	40.1	11.4	114	12	10	1.20
Ba-O	137.3	14.3	260	8	33	0.66
Zr-O	91.2	13.6	485	6	81	0.41
Nb-O	92.9	13.6	409	6	68	0.44
Ta-O	181.0	14.7	433	6	72	0.45
Ti-O	47.9	12.0	435	6	73	0.41
Al-O	27.0	10.0	402-317	4	101-79	0.32-0.36
Si-O	28.1	10.2	424	4	106	0.31

a)  $m_o$  mass of oxygen ion.

glasses given by Sun [10], i.e. values of the dissociation energies for the constituent oxides  $MO_x$  divided by the number of oxygen ions surrounding the cation M in the glasses, were used as the bond strength  $f'$  except for Nb-O and Ta-O bonds. The strengths of the Nb-O and Ta-O bonds were calculated by using the values of the heat of formation and heat of sublimation of the  $NbO_{2.5}$  and  $TaO_{2.5}$  [11] by the same procedure as that of Sun [10, 12].

It can be seen from table 4 that the relative wavelengths of the bands due to the stretching vibrations of all of the cation-oxygen ion bonds which are present in these aluminate glasses, are much longer than that of the Si-O bond. This explains why the cutoff wavelengths in the IR region of the present aluminate glasses are much longer than that of the silicate glasses. When preparing the glasses with high IR transmission, therefore, the use of cations, such as the  $Si^{4+}$  ion, which have low masses and form a strong bond with the oxygen ion should be avoided. The calculated data also show that the relative wavelength of the band due to the Al-O stretching vibration is the shortest of all those due to the cation-oxygen ion stretching vibrations in the present aluminate glasses. This suggests that the cutoff wavelength in the IR region of these glasses is determined by the Al-O stretching vibration. The fact that the cutoff wavelength of the calcium aluminate glass almost coincides with that of the present aluminate glasses (fig. 5) also suggests that the former is as well determined by the Al-O stretching vibration.

Figure 6 shows the relationship of the refractive indices versus Abbe numbers for commercially available optical glasses [13], in which the data for some of the present aluminate glasses are included for comparison. The refractive indices of the glasses are high relative to those Abbe numbers, because of the high content of  $TiO_2$  or  $Ta_2O_5$  [14].

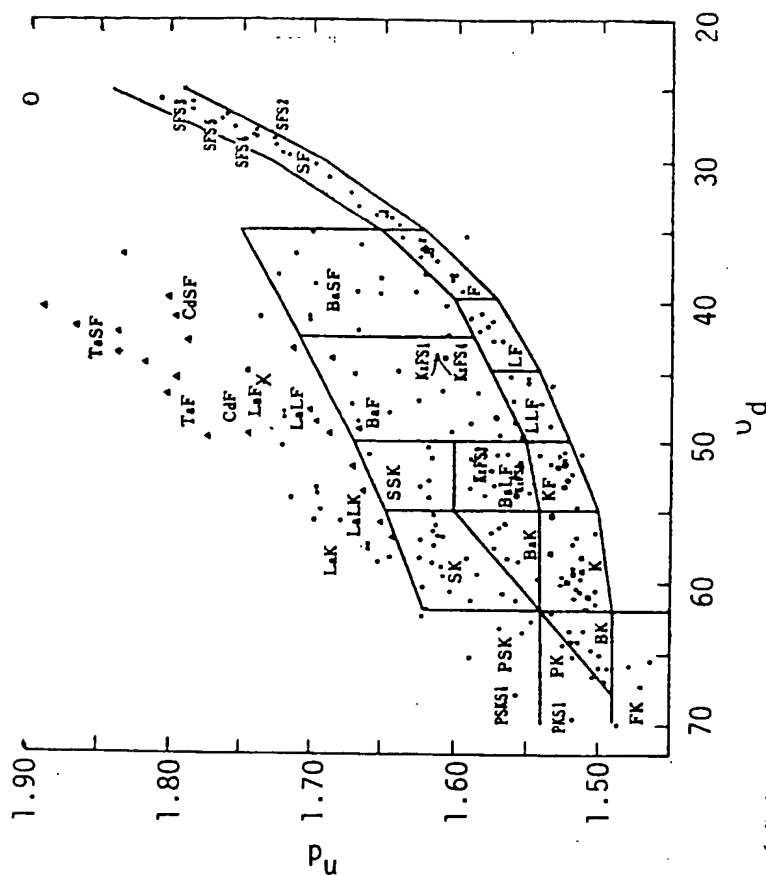


Fig. 6. Refractive indices and Abbe numbers of commercially available optical glasses and the present aluminate glasses. X glass 1, o glass 10.

#### 4. Summary

The new families of aluminate glasses obtained by the present authors showed high transmissions of visible and IR radiation ranging from 0.4 to about 6  $\mu m$ , as well as high refractive indices up to 2.0. Their physical and chemical properties such as glass-forming ability, softening temperature, hardness and hygroscopicity were comparable to conventional silicate glasses. These properties will be useful for IR applications.

The cause of the high IR transmission of the present aluminate glasses was interpreted in terms of the masses of the constituent cations and the single bond strengths of the cations with oxygen ions.

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